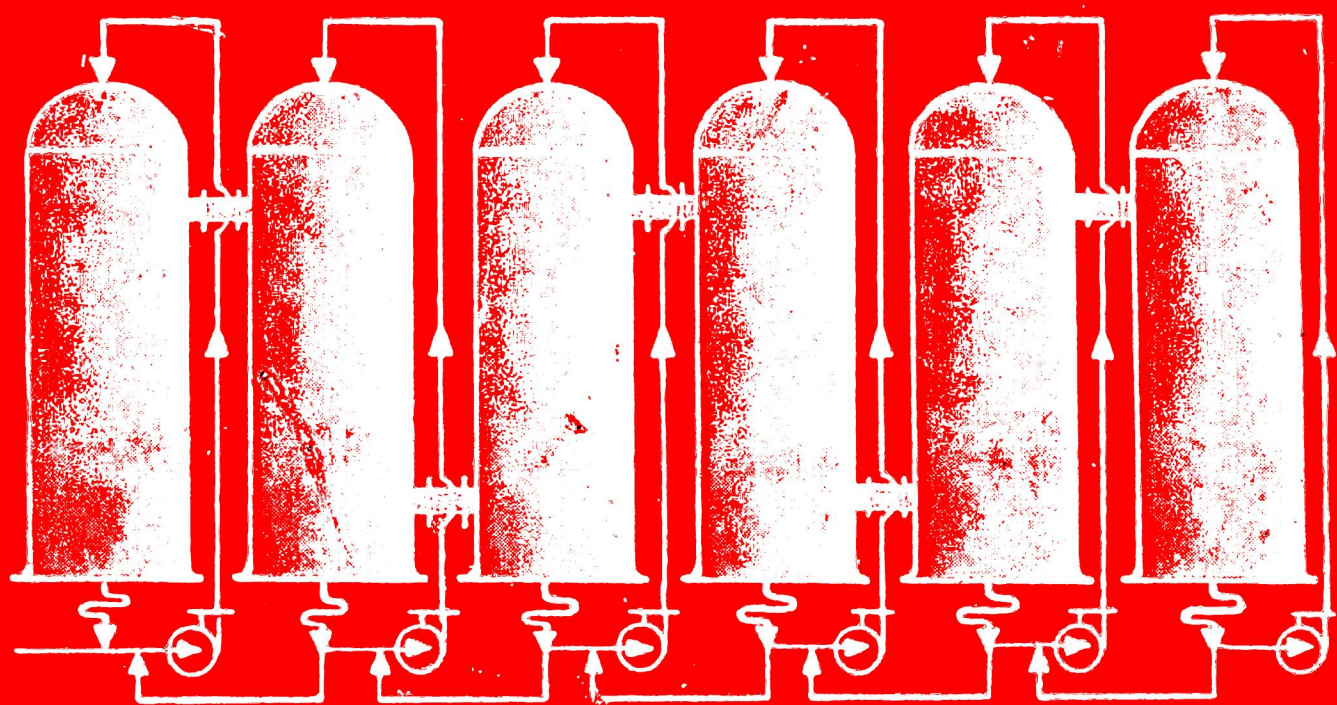


Chemical Technology 1

Edited
by

I. P. Mukhlyonov, D.Sc.



Mir Publishers

Chemical Technology

IN TWO PARTS

EDITED
BY I. P. MUKHLYONOV, D. Sc.

The Theoretical Foundations of Chemical Technology

PART I

**I. MUKHLYONOV
A. AVERBUKH
E. TUMARKINA
I. FURMER**

**Translated from the Russian
by GEORGE KOVAL**

MIR PUBLISHERS MOSCOW

И. П. МУХЛЕНОВ, А. Я. АВЕРБУХ,
Е. С. ТУМАРКИНА, И. Э. ФУРМЕР

ОБЩАЯ ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ

ЧАСТЬ 1

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА»

First published 1964

Second edition 1974

Third edition 1979

Revised from the 1977 Russian edition

На английском языке

© Издательство «Высшая школа», 1977 г.

© English translation, Mir Publishers, 1979



Growth of the chemical industry is proceeding by increasing the capacity of individual units, changeover to more advanced equipment at existing plants, introduction of new technological processes and extensive integration of production.

Modern chemical works usually have a complex combination of manufacturing processes united on the basis of integral utilization of the raw materials to produce a variety of intermediates, which are then used to make diverse final products. Quite often, however, the combination is based on the use of common basic technology in the production processes or on the use of common types of apparatus.

The growth of the chemical industry and the rapid increase in the number of manufacturing processes has been accompanied by what may be termed unification, i.e. similar basic technological procedures, apparatus and methods are used for manufacturing different chemical products.

It follows that chemical engineering graduates must be educated so as to be capable of managing a combination of diverse chemical manufacturing processes united in one factory, to be able to generalize operation results of a diversity of technological processes and to transplant best procedures and methods from one process to another. For this they must be equipped with broad knowledge and an understanding of general principles and typical methods of chemical technology. It follows that the course in Chemical Technology is of greatest importance in educating engineers for the modern chemical industry.

The basic theory of chemical technology has developed in parallel with the development of the chemical industry. Initially Chemical Technology dealt with all the various interrelated processes, both physical and chemical, which participate in manufacturing chemical products. In the following stage of development first of all the laws governing the physical processes were discovered and they separated out to form an independent technical science, known as Unit Processes and Unit Apparatus of Chemical Technology. It is concerned with hydraulic, thermal, diffusion, refrigeration and mechanical processes and apparatus. The study of chemical processes and apparatus remains as the chief objective of Chemical Technology.

However the number of chemical manufacturing processes continues its steady growth and the chemical industry now manufactures tens of thousands of products. To describe the production of

all of them in one college course would be impossible. On the other hand advances in science and technology have made it possible to formulate general relationships which apply to many different manufacturing processes since similar basic chemical methods, procedures and apparatus are used in different fields of the chemical industry. As a result, there is no need to study in detail a large number of chemical manufacturing processes in order to become an engineer with a broad technological outlook; knowledge of the general basic relationships, the most important industrial manufacturing processes and corresponding reactors is what is important. The connections between processes and the methods used in combining apparatus to form a production scheme can be studied by considering the manufacture of only a relatively small number of products. These should be selected from those most important to the national economy or related to the narrow field in which the future engineer wishes to specialize.

Chapters I, II and VI were written by I. Mukhlyonov; Chapter III by I. Furmer and I. Mukhlyonov; chapter IV by A. Averbukh; chapter V by E. Tumarkina; and chapter VII by I. Mukhlyonov, I. Furmer and E. Tumarkina.

The authors express their deep thanks to ass. professors A. Tubolkin, V. Soroko and V. Konovalov for valuable advice and critical remarks and would appreciate receiving any comments or suggestions from readers of the books.

Contents

Preface	5
Introduction	9
1. Importance of the Chemical Industry, Its Development and Growth . .	11
1. Importance of the Chemical Industry	11
2. New Developments in Chemical Technology	12
3. The Quality and Production Cost of Chemical Products . . .	16
2. Basic Principles of Chemical Technology	20
1. What is Meant by a Chemical Technological Process	20
2. Classification of Chemical Technological Processes	21
3. Chemical Equilibrium in Technological Processes	25
4. Rates of Technological Processes	34
5. Methods for Increasing the Process Rate	52
6. Technological Schemas	66
7. Designing Chemical Plants and Modelling Chemical Technological Processes	78
3. Chemical Reactors	90
1. Models of Ideal Plug-flow and Completely Mixed Continuous-action and Batch Reactors	95
2. Comparison of the Typical Features of Batch and Continuous-action Completely Mixed and Plug-flow Reactors	106
3. The Choice of a Reactor and Selectivity	112
4. Temperature Regimes of Reactors	118
5. Operating Stability of Reactors	128
6. Deviations of Real Reactors from Ideal Models	132
4. Homogeneous Processes and Reactors	136
1. Characteristic Features of Homogeneous Chemical Processes	136
2. Homogeneous Processes in the Gas Phase	139
3. Homogeneous Processes in the Liquid Phase	144
4. Homogeneous Process Basic Principles	145
5. Reactors for Homogeneous Processes	153
5. Heterogeneous Non-catalytic Processes and Reactors	159
1. Introduction	159
2. Gas-liquid (G-L) Systems	169
3. Gas-solid (G-S) Systems	185
4. Liquid-solid (L-S) Systems	215
5. Processes in Binary Solid, Two-phase Liquid, and Multiphase Systems	228

6. Catalytic Processes and Apparatus	231
1. The Importance of Catalysis and Its Field of Use	231
2. The Nature and Types of Catalysis	231
3. Homogeneous and Heterogeneous Catalysis	240
4. Properties of Solid Catalysts and Methods by Which They Are Made	254
5. Apparatus for Catalytic Processes	256
6. Basic Elements of Technological Calculations of Processes in Catalytic Reactors for Gas Mixtures	273
7. Photochemical, Radiochemical, Biochemical, Plasma-chemical and Ultrasonic Processes in Chemical Technology	281
7. Raw Materials and Energy for the Chemical Industry	287
1. The Characteristics of Raw Materials and Their Resources . .	287
2. Methods of Raw Material Concentration	391
3. Integral Utilization of Raw Materials and Combining Manu- facturing Processes	304
4. Replacement of Food Raw Materials by Non-edibles and Vege- table Materials by Mineral Ones	307
5. Water in the Chemical Industry	308
6. Energy for the Chemical Industry	316
Bibliography	321
Index	322

Introduction

Technology is the science which studies methods and processes for transforming naturally occurring raw materials into items of consumption and means of production.

A **processing method** is the group of operations to which a raw material is subjected en route to becoming a product. It can be described as a sequence of operations carried out in corresponding apparatus or machines. Such a sequence is known as a *technological scheme* (schema), or *flow diagram*. The technological scheme can be given by a textual discussion, or represented graphically as a sequence of interconnected machines and apparatus or sequence of interconnected operations. An operation may be carried out in one or in several pieces of apparatus (machines); it consists of a combination of different technological processes. In each apparatus either a single process or a group of processes takes place. In chemical reactors hydraulic, thermal, diffusion, and chemical processes usually take place together.

Technological processing may be mechanical or chemical in nature.

Mechanical technology deals with processes in which the shape, appearance or physical properties of a material are changed, whereas **chemical technology** deals with processes in which the composition, properties, and inner structure undergo basic alterations. This division is to a certain extent arbitrary, since changes in the appearance of a material are often accompanied by changes in composition and chemical properties. Thus, foundry processes are classed as mechanical ones, though when metals are cast chemical reactions also occur. On the other hand, chemical production processes are always accompanied by mechanical ones.

Chemical plants most often process naturally occurring raw materials into products consumed in industry: acids, alkalis, salts, syn-

thetic rubber, plastics, etc. Thus, common salt is the raw material used in making soda ash, but soda ash is principally not a consumer goods, but an industrial material employed, for instance, in manufacturing aluminium from bauxites or in making sodium hydroxide.

1. Importance of the Chemical Industry

The chemical industry manufactures thousands of kinds of products for use in the national economy, without which modern society could not exist. A few examples will be given to show the importance of the chemical industry.

Chemical processing of fossil fuels (coal, petroleum, natural gas, peat, and shale) yields such important products as coke, motor fuels, lubricants, combustible gases, and a large variety of organic substances. Without coke there could be no modern metallurgy and, consequently, all the industries in which metals are used, including engineering industry, would come to a standstill. Without gasoline, ligroin and other motor fuels airplanes and motor cars could not function. Combustible gases (smokeless and ash-free fuel) are of great importance in industry and for domestic uses. The organic chemicals made from natural gas, petroleum, coal, peat, and shale are starting materials for the manufacture of dyestuffs, varnishes, pharmaceuticals, alcohols, explosives, and other products used in almost all branches of industry and for domestic purposes. Of especial importance are resins—high-molecular synthetic materials—obtained from by-products of fuel processing and used in manufacturing plastics, synthetic fibres, synthetic rubber, etc.

There are innumerable other chemical products of great commercial value. Ammonia and nitric acid, manufactured from coal (or natural gas), water, and air, are used to produce fertilizers, various synthetics, and other products. Sulphuric acid made from naturally occurring sulphur or pyrites is employed in many fields of industry. It is used to transform minerals insoluble in water—apatite or phosphorite—into superphosphate or other phosphoric fertilizers. The non-ferrous metallurgy, engineering industry, textile, leather, food, and other industries are consumers of sulphuric acid and its salts. Lead batteries are used in vehicles.

Common salt is a raw material from which hydrochloric acid, soda ash, sodium hydroxide, and chlorine are manufactured, which in turn are used in producing aluminium, glass, soap, paper, cotton and wool fabrics, plastics, synthetic fibres, etc. Many useful products are obtained from wood; they include artificial silk and staple fibres, paper, plastics, smokeless powder, activated charcoal, acetic acid,

methyl and ethyl alcohols, turpentine, rosin, and acetone. Chemical methods are employed in producing the radioactive materials necessary for producing atomic energy.

What may be called "chemization" of the national economy is an important phenomenon. By "chemization" we mean the introduction and use of chemical methods, processes, and materials in industry and agriculture. Extensive penetration of chemistry into the various branches of industry leads to more rational methods of production, featured by absence of waste and utilization of all the components of the initial materials. Use of chemical methods and products in manufacturing processes is one of the important paths of technical progress in many industries, including metalworking.

A large number of chemical products are utilized as production aids in agriculture. Modern intensive farming is impossible without the use of inorganic fertilizers. The chemical industry also makes chemicals for combatting insects and plant diseases, and herbicides for destroying weeds.

2. New Developments in Chemical Technology

Growth of the chemical industry depends to a large extent on improvements in chemical technology. Development of the chemical industry is, in general, taking place along the same lines as in other fields of industry. The chief aims in technical progress are increased productivity, improved product quality, and lower production costs.

The principal ways in which chemical technology is developing are:

- (1) increased unit production capacity and equipment efficiency;
- (2) mechanization of processes where much labour is involved;
- (3) automation and remote control of industrial processes;
- (4) replacement of batch processes by continuous processes.

Increasing production capacity and intensifying operation of equipment is a highly important factor in technical progress. The most important operating index of machines, apparatus, shops or factories is their output. *Output (π) is defined as product manufactured (G), or raw material processed, per unit time τ [kg/hr or t/hr]:*

$$\pi = \frac{G}{\tau} \quad (1.1)$$

In many cases the amount is measured in volumetric units (V_p) and then π has the dimensions [m^3/hr]:

$$\pi = \frac{V_p}{\tau} \quad (1.2)$$

The production capacity of an apparatus can be raised by increasing either its size or the intensity at which it operates. Usually a

combination of both factors is employed. Increasing the size usually lowers the consumption of metals and other materials of construction per unit of reactor volume or unit of product. There is a corresponding reduction in unit cost of construction of buildings, structures, and auxiliary equipment. In general, costs of constructing plants and reconstructing existing plants drop. Increasing size or productivity of apparatus also lowers running costs. There is a decrease in losses of heat to the atmosphere, usually unit consumption of raw materials drops and, most important of all, labour productivity rises, since the staff size grows less than the production capacity does.

These economic factors have resulted in continuous growth of the capacity of new machines and chemical apparatus. For instance, the capacities of the basic reactors in sulphuric-acid and ammonia production has increased thirty times in the last twenty years in the USSR, and the output of adsorption units employed in organic chemical production has grown from tens of thousands to a million of cubic metres of processed gas per hour.

Increasing the production capacity of an apparatus without increasing its size, i.e. by intensifying its operation, is even more effective.

The operating intensity of an apparatus I can be defined as the ratio of the output (or production capacity) to a variable which describes the size of the apparatus. Intensity is commonly calculated by dividing apparatus capacity by its volume $V(\text{m}^3)$ or cross-sectional area $S(\text{m}^2)$

$$I = \frac{\pi}{V} = \frac{G}{\tau V} \quad (1.3)$$

$$I = \frac{V_p}{\tau V} \quad (1.4)$$

$$I = \frac{\pi}{S} = \frac{G}{\tau S} \quad (1.5)$$

$$I = \frac{V_p}{\tau S} \quad (1.6)$$

Intensification can be achieved in two ways:

- (1) by improving the design of machines or apparatus, and
- (2) by improving technological operations in apparatus of a given type.

Intensity of operation is proportional to the process rate and, therefore, in studies of the kinetics of technological processes the aim is to design an apparatus and find conditions which lead to maximum process rates.

An increase in operation intensity through improved or radically different design of machines or apparatus is usually accomplished by improving stirring of reaction components and increasing contact between interacting materials in different phases (solid, liquid, or gaseous). Improvements in design are often related to mechanization and automation of operation.

The most important technological means of intensifying apparatus operation are raising the temperature, pressure or concentration of reactants, combined with the use of catalysts and stirring. For some processes, however, an increase in the process rate can be achieved by lowering temperatures, maintaining a vacuum and keeping component concentrations low. As a result, temperatures beginning almost at absolute zero and ranging up to several thousand degrees are employed in chemical industries. Pressures in process apparatus lie between a lower limit close to absolute vacuum and an upper one of thousands of atmospheres. The use of very high temperatures, pressures, and voltages is limited by the properties of the materials of construction of the apparatus or by decomposition of reagents and, finally, by the cost of such methods of intensifying operations. Automation, mechanization and changeover from batch processes to continuous operation also usually result in higher operating intensity.

Mechanization is the replacement of manual labour by machine operations. Mechanization, as a rule, leads to higher productivity through increased operating intensity and reduced operating staff. Mechanization of processes involving much manual labour is one of the most important objectives of development not only in the chemical industry, but in all fields of industry and agriculture. In most branches of the chemical industry the basic operations are already highly mechanized, however we do not always find this to be true for such operations as feeding of materials to apparatus, discharging and moving products. Complete mechanization of these stages of production processes is at present a problem of great importance.

Automation is the introduction of instruments which make possible production without any direct participation of an operator; the functions of the operator are reduced to observation. Automation is mechanization at its highest level. It results in increased labour productivity, improved product quality and reduced production costs. For automation, as a rule, three principal components are necessary: a measuring element (or transducer), a controller, and a final control element. The measuring element, which measures one of the production variables, sends a signal to the controller, where measured and set values are compared and, if there is a difference between them, the controller sends a command-signal to the final control element.

In chemical industries the measured variables are usually temperature, concentration, rate of flow of gas (liquid) entering (or leaving) the apparatus. The task of the controller is to maintain the process variable at nearly constant value. Thus, by automation operating conditions are kept within permissible limits, without large deflections which often accompany manual control. To attain integrated automation of an entire production process, various types of

control instruments are used. In highly complicated cases when properties of the raw materials, temperatures, etc. can undergo sharp changes electronic computers are employed. Data from various measuring instruments are fed to an electronic computer which calculates optimum operating conditions and sends command-signals to the individual controllers. Thus, cybernetics is moving into the chemical field. The extensive introduction of automated systems for controlling overall production technology is one of the most important problems of the day.

In some cases fully automatic control is difficult or uneconomical to achieve and remote control may be used instead. Remote control is in effect partial automation in which measuring instruments and valve motors are used, but where the operator carries out the controller functions. The operator controls the process at a distance (from the control desk), switching valve motors on or off according to the readings of the measuring instruments. Centralized, or remote, control may also be a supplementary part of an automated system.

The replacement of batch processes by continuous processes is a feature of technical progress in the chemical industry.

A batch process is one in which measured portions of the raw materials are introduced into apparatus, where they undergo a number of stages of treatment, after which all the products formed are discharged. Thus, there is a definite time interval between the charging of the raw materials and the removal of the products. The apparatus is idle during the charging and discharging stages. These operations require much manual labour. Mechanization of loading and unloading is more difficult to achieve here than in continuous processes, since more powerful, intermittently operating mechanisms are necessary. Automation of a batch process is even more complex than in the case of a continuous process. This is because the variables which are most often controlled, i.e. temperature, pressure, and concentration, change during the reaction process. Usually the temperature and pressure rise at first and then drop towards the end of the reaction; the concentrations of the initial reactants continuously decrease, but the rate of decrease changes. Production is lower in the period when the operating conditions are being established. Batch processes are difficult to control, and often the quality of the product depends markedly on the operating conditions. The duration of the production cycle, i.e. the time required for carrying out a batch process, is always greater than the duration of the corresponding continuous process and power consumption is also larger. These factors have created a tendency to replace batch processes by continuous ones.

Continuous processes are processes in which the raw materials are fed and the products are removed continuously (or in consecutive portions) over a long period of time. In this case the basic technolo-

gical processes, ancillary processes, and transportation of the products all take place concurrently. There is no idle equipment and apparatus productivity is higher. At any single spot in the apparatus the temperature, concentrations, and pressure do not change with time, and the conditions in the apparatus can more easily be controlled; it is easier to mechanize charging and discharging, to achieve full automation. The products manufactured in continuous operation processes are usually of higher quality; waste heat and waste products (e.g. gases) can more readily be utilized, since they are evolved at a steadier rate.

Most chemical processes are now carried out in continuously operating equipment, and remaining batch operations are gradually being replaced by continuous ones. At the present time, however not all processes can be switched over to continuous operation: in some cases this would result in low quality of the products (e.g. for carbonization); in others rational equipment necessary for mechanization and automation have not as yet been developed, especially in cases where low-capacity, small-scale equipment is used.

When continuous and batch operations are compared, one should remember that the mean concentration of reactants is lower in continuous-operation flow-through reactors than in batch reactors which leads to lower reaction intensity (see Chapter 2).

The tendencies mentioned above are interrelated and interdependent; therefore, the various means for obtaining higher operation intensity should be used together to achieve the desired end. The technical steps should be supplemented and reinforced by improved organization and management.

Atomic-energy techniques provide a new, powerful means for increasing operation efficiency in a number of manufacturing processes. Extremely high temperatures—hundreds of thousands and even millions of degrees—can be reached by using atomic energy; radiation accelerates many chemical processes, by using radioactive isotopes automation of a number of processes is made much easier, etc.

3. The Quality and Production Cost of Chemical Products

High intensity of industrial processes achieved by progress in technology must be accompanied by high product quality, minimum cost of production and good working conditions. In designing apparatus and determining the operating values of the process variables such conditions are therefore chosen at which a rational combination of all these factors is attained. Operating conditions at which the optimal process rate is highest, but resulting in a lowering of product quality, a rise in cost of production or in poor working conditions should definitely be avoided.

The quality of a chemical product is usually determined by its purity, or the concentration in it of the basic component. For high-molecular compounds the molecular structure and the physicochemical properties which depend on it are also important. The manufacture of pure or concentrated products is of importance not only with respect to the quality of the end products, i.e. items of consumption. The use of high-concentration products (to be more exact, intermediates) intensifies the processes in which they are employed as starting materials or means of production, and it should be remembered that the products of the chemical industry are to a very large extent starting materials or means of production, rather than consumer goods. Increasing the concentration of the useful component in the chemical products of multitonnage processes is also important from the point of view of transportation costs. Thus for instance, the content of useful components in mineral fertilizers is usually from 15 to 50 per cent. Consequently when fertilizer production exceeds 100 million tons per year, approximately 70 million tons of ballast are transported over distances of hundreds of kilometres. For these reasons the trend is toward higher product concentrations in the inorganic fertilizer, acid, alkali, and many other manufacturing industries.

Cost of production is a question studied in economics courses. We shall mention here only the basic factors involved. The sums spent in producing and distributing a product are called its *full cost*. The expenditures directly connected with manufacturing the product make up the *shop cost*. The ratios between the various items of expenditure show the cost structure.

Shop cost results from the following main items: (1) raw materials, intermediates, and basic materials* directly involved in the chemical reactions of the manufacturing process; (2) fuel and power for technological use; (3) wages of workers involved in the basic production processes; (4) depreciation funds allotted to cover wear and deterioration of the principal capital assets: buildings, structures, equipment, etc.; (5) shop expenses, which cover maintenance and repairs of the principal capital assets (including wages of workers of auxiliary and repair services) and also wages of shop-management personnel and labour protection and industrial safety measures; (6) general plant expenses.

* In computing the cost initial materials which have not been subjected to processing are called raw materials. Initial materials subjected to preliminary industrial processing at the manufacturing plant are called intermediates. Initial materials subjected to preliminary industrial processing at other manufacturing plants are called basic materials. In some textbooks basic materials and semifinished products used in a manufacturing process are often called *raw materials* or *intermediates* of the process.

The value of by-products obtained from the initial materials is usually subtracted from the production costs of the basic product. In determining cost of production, i.e. expenditure per unit finished product, it is necessary to calculate the values of process consumption factors for the raw materials, fuel, and power expressed in natural units (e.g. tons of raw material per ton of product), and then calculate the production cost, using the known prices of the materials, and taking into account the other costs.

The relative weight of various items of cost differs widely for various branches of the chemical industry. The most important item is usually the cost of raw materials, in an average case it comprises 60 to 70 per cent of the total production cost. Ordinarily, fuel and power requirements give rise to about 10 per cent of the cost; however, in electrothermal and electrochemical processes expenditures on electrical energy are one of the main items of cost.

Wages of basic operators due to the high degree of automation and mechanization of the continuous production processes prevalent in the chemical industry amount on the average to only about 4 per cent of the total cost. In a number of chemical manufacturing plants, however, the share of wages may be as high as 20 per cent. Depreciation costs are usually 3 to 4 per cent of the total cost of production.

An analysis of the structure of the cost of production shows where cost reductions can be found. Methods and operating conditions which lead to low material consumption factors should be used. Ways of employing new inexpensive raw materials should be developed. Integral utilization of all the constituents of the initial materials, their transformation into products of value is a powerful means for lowering the cost of production of the end product.

Intensifying operation is one of the most general methods used for lowering the cost of production, since effectively accomplished intensification, for instance by a change-over from batch to continuous operation, or through automation, may lower expenditures on all the items entering into the calculated cost. However, in some cases, intensification may lead to increased consumption factors for materials and fuel, along with the decrease in expenditures on other items, or to increased depreciation; in this case it is the overall calculated cost that can show whether intensification is worthwhile. The effect of the measures leading to lower product costs on its quality and working conditions must always be taken into account.

Improving working conditions. People working in the chemical industry often have to deal with dangerous, toxic gases, liquids and dusts, and with high temperatures and pressures. In the USSR special laws and regulations governing working conditions and industrial safety measures ensure the use of hermetically sealed apparatus, good ventilation, thermal insulation of hot surfaces, etc. There are a great variety of hazards that may arise in the different branches of the

hemical industry: explosions, injury by machines, burns, and acute poisoning. To reduce these hazards, compulsory safety regulations are introduced, which require installation of guards and other safety devices. Such measures and devices are studied in courses on industrial safety. In designing apparatus and plants the choice of apparatus and operating conditions should reduce hazards to a minimum. Mechanization and automation aid in this respect. There is a safety engineer at every chemical plant whose special function is to control operating conditions and observance of safety rules.

In recent years large technological systems, apparatus and reactors, with capacities exceeding those which were formerly most common by 10 times or more, have been designed and built. Such an increase in production capacity makes it easier to introduce automation and to integrate measures for increasing labour productivity, lowering product costs and improving working conditions.

1. What Is Meant by a Chemical Technological Process

Chemical technology studies the aggregate of physical and chemical phenomena which together comprise a technological process. Processes of chemical technology usually embody three interrelated elementary processes (stages): (1) *transfer of reaction components to the reaction zone*; (2) *chemical reactions*; (3) *removal of the products from the reaction zone*.

1. Transfer of reaction components to the reaction zone may be either by molecular diffusion or by convection. When mixing is very strong transfer by convection is often called turbulent diffusion. In two-phase and other multiphase systems* reaction components may be supplied to the reaction zone by absorption, adsorption or desorption of gases, by condensation of a vapour, by melting solids or by dissolving them in liquids, and by evaporation of liquids or sublimation of solids. Interphase mass transfer is a complex process involving diffusion.

2. Chemical reactions are the second step of chemical processes. Usually several consecutive (and sometimes also parallel) chemical reactions take place in a system to yield the principal product. There may also be a number of side reactions between starting materials and impurities, which are always present in the materials in some amounts. As a result, together with the principal product reactions yield by-products (products of value) and waste products (products of no significant value). These by-products and waste products may be formed in the course of the basic reactions or they may result from secondary reactions between principal initial materials or between principal materials and impurities. Usually when production processes are subjected to an analysis not all the reactions are taken into account, but only those which significantly affect the amount or the quality of the final product.

3. Removal of the products from the reaction zone may also occur by diffusion, convection or transfer of a substance from one phase state (gas, liquid, solid) to another.

* Systems are groups of substances participating in chemical or physical interaction. A phase is all the homogeneous portions of a system similar in composition and in physical and chemical properties and separated from other parts of the system by an interface.

The overall rate of a process is in some cases determined by the rate of one of these three elementary processes—when it is much lower than the others—but often all the elementary-process rates are comparable. If the chemical reaction is the slowest of the elementary processes, and it is the chemical reaction that limits the overall rate, it is said that the process is kinetics controlled; and in such cases chemical engineers utilize factors which affect the reaction rate (concentration of starting materials, temperature, catalysts, etc.) to cut process time. If the overall rate is limited by the rate of supplying reactants to the reaction zone or by the rate of removing reaction products, then the process is said to be diffusion controlled. The diffusion rate is then increased by agitation (to intensify turbulence in the reaction system), raising temperatures or concentrations, by a change-over from a multiphase process system to a single-phase one, etc. If the rates of all the elementary processes are approximately equal, then such factors should be utilized to accelerate the process, which affect both the rate of diffusion and the reaction rate, i.e. the concentration of the reactants and the temperature should be raised.

By applying the basic principles of chemical engineering one can choose the most effective combinations of chemical and physical conditions for carrying out a given process, i.e. such conditions which result in high process intensity, high product yield, good product quality. The chemical engineer employs these basic principles both in analysing a production process to improve its operation, and, especially, in designing new production processes.

2. The Classification of Chemical Technological Processes

All processes of chemical technology can be classified, first of all, either as chemical, which include chemical reactions, or physical processes. This course is concerned with industrial chemical processes. Chemical reactions are always the most important stage in an industrial chemical process. The chemical reactions of a technological process may be simple, complex-parallel or complex-consecutive in nature. In describing the various types of industrial chemical processes reactions are also classed in accordance with the nature of the reaction between components as oxidation-reduction (homolytic) or acid-basic (heterolytic) ones. Chemical reactions and mass transfer may be reversible or irreversible and the technological process in which they are involved is classified accordingly. A distinction must be made between processes which are kinetics controlled and those which are diffusion controlled. It is very difficult to classify in such a way processes in heterogeneous systems, especially when a component of a gas or liquid mixture reacts with the surface of a solid porous material. In such processes, depending on which stage is the

controlling one, the following kinds are observed: external diffusion, intermediate between external diffusion and internal diffusion, internal diffusion (within the pores of the solid), internal-intermediate,⁷ and kinetics controlled. These are the most important cases of heterogeneous catalytic processes.

In complex cases the classification employed depends on the way it is to be used. Determining the class of a technological process is very important for selecting an optimal technological regime.

The aggregate of basic variables (parameters) which affect the rate of a process, and the yield and quality of the product is called the technological regime. For most chemical technological processes the basic regime variables are the temperature, pressure, catalyst used and its activity, the concentrations of the reacting substances, the method used for agitating the reagents and the degree of mixing. For some types of chemical technological processes other regime variables, which are not typical for most processes, are of prime importance; for example, electrochemical processes depend on voltage and current densities and radiation-chemistry processes, on the radiation level.

The variables of a technological regime determine the design of reactors employed. Since optimal values of the technological regime variables correspond to maximum productivity of apparatus and of operating personnel, the nature of the technological regime and the levels of the variables serve as a basis for classification of chemical technological processes. All the technological regime variables are, however, interconnected and depend, to a large degree, on one another. A significant change in one of the variables results in a sharp change in the optimal values of other regime variables. A strict classification of technological processes based on the values of all possible regime parameters would, therefore, be extremely complex and of little value in a general course on chemical technology. The variables which are of prime importance should be used. The method of agitation and the degree of mixing of reactants have a marked effect on the design of reactors and on the process rates. In turn, the method employed and the intensity of mixing of reactants depend on their phase state: it is above all the phase state of the substances being treated which determines the method of processing and the basic design features of the apparatus. Therefore, in the study of basic principles of chemical technology, *the classification of processes and the corresponding reactors is based primarily on the phase state of the reacting substances.*

With respect to this feature all systems of reacting substances and the corresponding technological processes employed are classed as single-state (homogeneous) or multistate (heterogeneous) processes.

Homogeneous systems are such in which all the reacting substances are in the same phase: gas (G), liquid (L), or solid (S). In homogeneous systems reactions usually occur at higher rates than in hetero-

geneous ones, the overall mechanism of the technological process is simpler and it is easier to control the process. Chemical engineers, therefore, often seek to organize processes on a homogeneous basis, i.e. to convert solid reactants, or at least one of them, to the liquid state by fusion or dissolution; for the same purpose gases are absorbed or condensed.

Heterogeneous systems include two or more phases*. Possible two-phase systems are: gas-liquid; gas-solid; liquid-liquid (immiscible); liquid-solid; and solid-solid. In industrial practice G-L, G-S, L-S systems are the most common. Industrial processes often occur in multiphase (more than two phases) heterogeneous systems such as G-L-S, G-S-S, L-S-S, G-L-S-S**, etc. Heterogeneous processes are more common in industrial practice than homogeneous ones. As a rule, the heterogeneous stage of a process (mass transfer) is of a diffusional nature, and the chemical reaction is of a homogeneous one in the gas or the liquid phase. In many industrial processes, however, heterogeneous reactions which determine the overall process rate occur at a G-S, G-L, L-S interface. Examples of heterogeneous reactions are the burning (oxidation) of solids and liquids, and dissolution of metals and minerals in acids and alkalis.

According to the level of the regime variables processes can be divided into low-temperature and high-temperature, proceeding under vacuum, at normal or at high pressures, with a high or low concentration of the starting materials, etc. Such a classification is employed in some books devoted to individual chemical manufacturing processes, but is too complex for a general course in chemical technology.

According to the pattern of change in the processes with time apparatus and the processes taking place in them are divided into batch and continuous ones. Continuous-action reactors are also called flow-through reactors, since there is a constant stream of reactants through them.

According to the hydrodynamic regime, two limiting cases of mixing the reacting components with the reaction products are distinguished: (1) complete mixing, in which agitation is so intense that the concentration of the reagents in a flow-through reactor is uniform over the entire volume of the apparatus from the point of entrance of the initial mixture to the exit of the product mixture; in this case the mean concentration equals the final one; (2) ideal plug flow, in which the initial mixture does not mix with the reaction

* Phases of a heterogeneous system may also be uniform or non-uniform in composition and properties.

** In chemical technology, the term solids is used for all materials whose particles (atoms, ions, molecules) are permanently fixed with respect to each other, including amorphous bodies (for instance, glass), which, according to the physicochemical definition, are really supercooled liquids.

products but flows laminarily through the entire length or height of the apparatus. In the latter reactors there is a gradual change in the concentration in the direction of the reactant stream, whereas at ideal mixing there is no concentration gradient over the reaction volume.

In industrial continuous-action reactors the degree of mixing is always lower than in apparatus with ideal mixing and higher than in apparatus with ideal plug flow. In some reactors, however, the mixing pattern is close to one or the other of the limiting cases.

According to the pattern of the thermal regime flow-through reactors are divided into isothermic, adiabatic, and programme-controlled (polythermic) ones.

In isothermic reactors the temperature is constant throughout the entire reaction volume, since for an exothermic reaction the heat is removed or uniformly distributed throughout the reaction volume, whereas in endothermic processes heat consumed is completely balanced by heat supplied. An ideal isothermic regime is only possible in a completely mixed reactor.

In adiabatic reactors no heat is withdrawn or supplied, but all the heat of the reaction accumulates in the reactant stream. A truly adiabatic regime exists only in reactors with ideal plug flow at complete isolation from the surrounding medium. In these reactors the temperature along the reactant mixture stream is directly, or inversely, proportional to the degree of conversion of the starting material into the product.

In programme-controlled reactors the heat of the reaction is only partially withdrawn from the reaction zone, or partially balanced by heat supplied in endothermic processes, according to preliminary design calculations of the apparatus. Consequently, the temperature along the length or height of the reaction space changes non-uniformly and the temperature pattern corresponds to a curve whose form was determined in the preliminary calculations (programme); it is controlled by changing the variables of the technological regime. Industrial reactors operate ordinarily in polythermic regimes but in some cases they may approach an isothermic or an adiabatic one.

Chemical conversions are always accompanied to a larger or smaller degree by thermal processes. According to the sign of the heat effect of a process it is classed as exothermic or endothermic. Such a division is especially important from the point of view of the influence of the heat effect on the equilibrium and rate of reversible reactions. In many industrial processes the nature of the heat effect of the reactions determines the production flow scheme and reactor design employed.

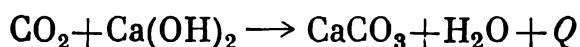
In heterogeneous systems a distinction is made between cocurrent, countercurrent and crosscurrent processes. Such a classification is necessary in determining the pattern of change of the driving force of a process along the height (length) of a reactor.

It follows that even the simplified classification of processes used in a general course on chemical technology must be quite complex, to reflect the various angles of view from which the diverse chemical technological processes which exist in industry must be studied.

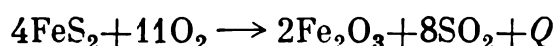
Basic objects of study in chemical technology are the equilibria and rates of chemical technological processes. The laws which govern equilibria and process rates differ very significantly for homogeneous and heterogeneous systems.

3. Chemical Equilibrium in Technological Processes

Chemical processes may be *reversible* or *irreversible*. Irreversible processes proceed in one direction only. Chemical reactions are, as a rule, reversible in the respect that, depending on conditions, they may proceed in one direction or in the other. But under typical industrial conditions most chemical reactions are practically irreversible. For example, the reaction



under the conditions used in purifying a gas mixture of CO_2 by scrubbing it with milk of lime is practically irreversible. Many complex reactions which are an aggregate of a number of stages are irreversible, for example, the reaction of pyrite combustion:



In heterogeneous systems, *processes in which transfer of mass or heat from one phase to another is possible in both directions are known as reversible ones.*

All reversible chemical technological processes move toward an equilibrium, at which the rates of the direct and reverse processes become equal and, as a result, the ratio of the components in the reacting system remains unchanged unless there is a change in the external conditions. If there is a change in the temperature, pressure, or concentration of one of the components (or its molar volume, which is the inverse of the concentration) the equilibrium is disturbed, and spontaneous diffusional and chemical processes occur in the system which re-establish equilibrium in new conditions. The second law of thermodynamics, in its general form, is applicable to chemical equilibria, i.e. *one of the conditions for the existence of chemical equilibrium in an isolated system is maximum entropy S .* At equilibrium there is no further increase of entropy, a feature of all spontaneous processes, i.e. $dS = 0$.

Qualitatively the effect of the basic technological regime variables on the equilibrium in homogeneous and heterogeneous systems can be determined by applying Le Chatelier's principle, which expresses the second law of thermodynamics. According to the Le Chatelier

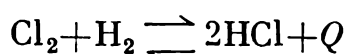
principle, after the equilibrium of a system is disturbed from the outside, the direction of the change in it is such as to counteract the effect which disturbed the equilibrium.

Let us consider an example of the application of the Le Chatelier principle to an exothermic reaction:



where m , n and p are the number of moles of A, B and D, and Q is the heat of the reaction. Let the volumes of the substances involved be denoted by V and let us consider a case where $V_A + V_B > V_D$, i.e. where the reaction results in a decrease in volume.*

The basic factors which effect the chemical equilibrium are the temperature t , pressure P , and concentrations of the reacting substances C_A , C_B and C_D . To shift the equilibrium to the right, i.e. to increase the amount of the product (to raise the yield), according to Le Chatelier's principle it is necessary to lower the temperature and the concentration of the reaction product (C_D), i.e. to remove the product from the reaction zone, raise the pressure P or increase the amounts of reactants C_A and C_B in the reaction zone. An increase in C_A will result in fuller conversion of B, and an increase in C_B in fuller conversion of A. This effect is often utilized in industrial chemistry. For instance, in synthesizing hydrogen chloride by the overall reaction



the presence of chlorine in the hydrogen chloride is undesirable (it contaminates the hydrochloric acid), whereas the presence of hydrogen does not create any difficulties. A gas mixture is therefore employed with an excess of hydrogen in it and a gas is produced which contains practically no chlorine.

In applying Le Chatelier's principle to a heterogeneous exothermic process of absorption of a component of a gas mixture with a liquid we find that the equilibrium concentration of the gas in the liquid, or the equilibrium degree of absorption of the gaseous component (product yield), will grow with a decrease in temperature, with an increase in the total pressure, and also with a decrease in the vapour pressure of the absorbed component. The vapour pressure can be lowered by removing the product from the absorption zone, for instance, by precipitating it in the form of solid crystals**. A rise in concentra-

* Reaction (2.1) is the basic type of reaction in many industrial processes described in the following chapters of this book, for instance, oxidation of sulphur dioxide, absorption of sulphur trioxide, syntheses of ammonia, hydrogen chloride, high polymers, and many other organic and inorganic products. It will therefore be used as a model.

** Thus, for absorbing carbon dioxide a solvent can be selected which gives a crystalline precipitate with CO_2 , for example, milk of lime Ca(OH)_2 , which yields a CaCO_3 precipitate.

tion (partial vapour pressure) of the component being absorbed in the gas mixture increases the equilibrium concentration in the liquid, however the degree of absorption does not necessarily grow in this case.

The solubility of a solid crystalline substance in a liquid, according to Le Chatelier's principle, is raised by an increase in temperature if the process is endothermic (the amount of energy required to disrupt the crystal lattice is ordinarily larger than the heat of solution of the molecules). Pressure usually has no effect on equilibrium, because the change in volume caused by increasing the pressure is insignificant.

The equilibrium constant is used to quantitatively characterize the mobile equilibrium. In physical chemistry the equilibrium constant is defined as a thermodynamic value; however, it may also be derived from the law of mass action, according to which the instantaneous rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reacting substances. For reaction (2.1) the rate of the forward reaction is

$$\vec{u}_1 = k_1 [A]^m [B]^n \quad (2.2)$$

and the rate of the reverse reaction is

$$\overleftarrow{u}_2 = k_2 [D]^p \quad (2.3)$$

where k_1 and k_2 are the velocity constants of the forward and reverse reactions; $[A]$, $[B]$ and $[D]$ are molar concentrations (or partial vapour pressures) of the reagents at the given moment, i.e. values which change during the process.

The equilibrium constant K is defined as the ratio of the velocity constant of the forward reaction to the velocity constant of the reverse reaction at equilibrium, i.e. when $\vec{u}_1 = \overleftarrow{u}_2$, or

$$k_1 [A^*]^m [B^*]^n = k_2 [D^*]^p \quad (2.4)$$

from which

$$K = \frac{k_1}{k_2} = \frac{[D^*]^p}{[A^*]^m [B^*]^n} \quad (2.5)$$

where $[A^*]$, $[B^*]$ and $[D^*]$ are concentrations or partial pressures of the reactants at equilibrium.

For gases K may be derived employing partial vapour pressures p of the reactants (say, in atmospheres), their concentrations C (for instance, in moles per cubic metre) or, finally, their mole fractions N . The respective equilibrium constants are then K_p , K_C , K_N . They are interrelated as follows:

$$K_p = K_C (RT)^{\Delta N} \quad (2.6)$$

$$K_p = K_N P^{\Delta N} \quad (2.6a)$$

where P is the total pressure of the gas mixture and ΔN , the increment in the number of moles of gas resulting from the reaction. For the model reaction (2.1)

$$\Delta N = p - (m + n) \quad (2.7)$$

To obtain dimensionless K values relative values are substituted into the equation; for instance, the ratio of the partial vapour pressure (atm) to the standard pressure, which is 1 atm. For solutions, either molar concentrations or ion concentrations may be used. Equation (2.5) is not employed for calculating the value of the equilibrium constant K , since the equilibrium concentrations are usually unknown; they are determined for known concentrations of the initial products from the K value. Equilibrium constants for various reactions, determined by experiment or calculated for specified conditions of temperature and pressure, are given in tables, or they can be determined from nomograms, contained in relevant textbooks and reference books. To find the K value from experimental data, it is expressed as a function of the product yield.

The product yield is the ratio of the actual amount of product obtained, G_a , to the maximum amount, G_{\max} , which could be obtained from a given quantity of a starting material:

$$x = \frac{G_a}{G_{\max}} \quad (2.8)$$

For chemical reactions the maximum amount of the product is determined from the reaction equation with reference to the principal starting material. The component of the reaction mixture which costs the most and of which there is usually a deficiency with respect to the stoichiometric amount is, as a rule, considered to be the basic component. Thus, for the industrially important reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ SO_2 is assumed to be the principal component since the other reactant—oxygen—is contained in air and is lower in cost. The same holds true for all of the many oxidation reactions in which oxygen of the air is employed, and where oxygen is always taken in excess. For ethylene hydration,



ethylene is assumed to be the basic component. Water is of course not considered to be the principal initial material; it is taken in excess in most processes of hydration, hydrolysis and conversion with steam. For interphase mass-transfer processes (absorption, desorption, evaporation, etc.) the maximum amount is equal to the entire amount of the substance present in the contributing phase (for absorption, for instance in the gas). The product yield expressed in the above way when applied to chemical reactions is usually called the *degree of conversion*. In mass-transfer processes the yield so expressed

is known as the *degree of interphase transfer*, for example the absorption degree, desorption degree, etc.

The degree of conversion or of interphase transfer can be expressed (as the name suggests) through the ratio of the amount of the principal substance consumed to its amount at the beginning of the process G_1 :

$$x = \frac{G_1 - G_f}{G_1} \quad (2.9)$$

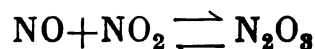
where G_f is the amount of starting material which remains (in the contributing phase of mass transfer) at the end of the process. Equations (2.8) and (2.9) can be used for calculating the degree of conversion or any one of the starting materials in a homogeneous reaction.

If we substitute in the numerator of equation (2.8) the amount of the product at equilibrium, then the yield is known as the *equilibrium yield*, x_e , or *theoretical yield*, x_t . For irreversible processes, since chemical conversion or mass transfer from one phase to another is complete, $x_{e(t)} = 1$. For reversible processes the equilibrium yield, which corresponds to equilibrium degree of conversion, is always less than unity ($x_e < 1$), since when equilibrium is established conversion of the starting material into the product is incomplete.

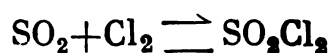
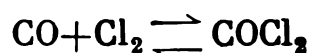
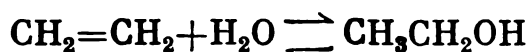
The equilibrium yield x_e is usually calculated using equilibrium constant (K) values, which are listed in tables in the literature. On the other hand, the values of K in the tables were in many cases calculated using the same formulas from equilibrium product yields determined by experiment. The form of the equation employed for computing the equilibrium constant from the equilibrium yield of the product, x_e , depends on the type of reaction. We shall derive an equation for a gas-phase reaction of the type



A number of industrial chemical processes proceed by reactions of this type, for instance association of nitric oxide and nitrogen dioxide in manufacturing nitric acid



and synthesis of ethyl alcohol, phosgene, and sulphuryl chloride:



If x_e is used to denote the equilibrium yield of product D, expressed as a fraction, p_A^* , p_B^* and p_D^* —the partial vapour pressures of the starting materials A, B and of the product D in the equilibrium

gas mixture, then for the stoichiometric ratio of the starting materials in a pure gas mixture at equilibrium, we can write

$$P = p_A^* + p_B^* + p_D^* \quad (2.10)$$

where P is the total pressure. According to (2.8)

$$x_e = \frac{G_D}{G_{\max}} = \frac{p_D^*}{P} \quad (2.11)$$

$$\frac{p_A^*}{P} + \frac{p_B^*}{P} = 1 - x_e \quad \text{and} \quad \frac{p_A^*}{P} = \frac{p_B^*}{P} = \frac{1 - x_e}{2} \quad (2.12)$$

The equilibrium constant, according to (2.5), is:

$$K_p = \frac{p_D^*}{p_A^* p_B^*} \quad (2.13)$$

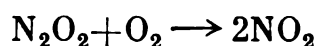
By substituting the partial vapour pressures from (2.11) and (2.12) into (2.13) we obtain

$$K_p = \frac{x_e P}{\left(\frac{1 - x_e}{2}\right)^2 P^2} = \frac{4x_e}{(1 - x_e)^2 P} \quad (2.14)$$

For reactions whose equation can be expressed by the model



for instance, for synthesis of hydrogen chloride or for oxidation of the nitric oxide dimer:



we can write:

$$x_e = \frac{p_D^*}{P}, \quad \frac{1 - x_e}{2} = \frac{p_A^*}{P}, \quad \frac{1 - x_e}{2} = \frac{p_B^*}{P}$$

$$K_p = \frac{(p_D^*)^2}{p_A^* p_B^*} = \frac{x_e^2 P^2}{\left(\frac{1 - x_e}{2}\right)^2 P^2} = \frac{4x_e^2}{(1 - x_e)^2} \quad (2.15)$$

In this way an equation can be obtained which relates x_e and K_p for any reversible reaction. By solving equations (2.14) and (2.15) with respect to x_e it can be shown that according to Le Chatelier's principle in the first case the yield increases with an increase in pressure and in the second case it does not depend on the pressure.

Equations (2.2) to (2.15), for the rate or the equilibrium of reactions are valid only for simple reactions between ideal gases or for components of infinitely dilute solutions and for ratios of the reactants close to stoichiometric ones. When we consider real conditions it is necessary to use fugacities and activities of the reacting components.

The stoichiometric coefficients in the formal equations of chemical reactions which in most cases express only the overall numerical

ratios between the starting materials and the products, necessary for drawing up material balances of the process, should not be considered to be true ones. The real mechanism of the process should be sought; the slowest, limiting stages found and the true reaction order determined. This order should be used in determining the values of the exponents in equations of types (2.2) and (2.3). For example, the reaction of nitric oxide oxidation in manufacturing nitric acid, and also sulphuric acid by the nitrous method, is usually described by the overall reaction equation:



Judging by the molarity of reaction (a), the rate of the direct oxidation process should be given by a third-order rate equation, i.e. with the sum of the exponents equal to 3:

$$\vec{u} = k_1 C_{\text{NO}}^2 C_{\text{O}_2} \quad (2.16)$$

where C_{NO} and C_{O_2} are the concentrations of the nitric oxide and oxygen in the reacting mixture.

The equilibrium constant of reaction (a) is described by the equation

$$K = \frac{(C_{\text{D}}^*)^p}{(C_{\text{A}}^*)^m (C_{\text{B}}^*)^n} = \frac{(C_{\text{NO}_2}^*)^2}{(C_{\text{NO}}^*)^2 C_{\text{O}_2}^*} \quad (2.17)$$

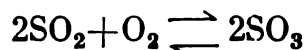
But actually, the reaction proceeds in two successive stages:



the rate of each is given by a second-order rate equation; the overall process rate is also expressed by a second-order rate equation. Under industrial conditions the overall process rate is limited by the low value of the equilibrium constant of reaction (b). Consequently the equilibrium of the entire process does not correspond to equation (2.17) but to

$$K = \frac{C_{\text{N}_2\text{O}_2}^*}{(C_{\text{NO}}^*)^2} \quad (2.18)$$

For catalytic processes the reaction order is almost always lower than the molarity of the reaction equation. Thus, for non-catalytic oxidation of sulphur dioxide

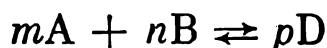


the reaction is of the third order ($n = 3$); when oxidation is carried out over a catalyst, depending on its activity, the reaction order, n , drops with an increase in the catalyst activity. For low-activity iron-

oxide catalysts, $n = 2.5$, for more active vanadium ones, $n = 1.8$, and for the most active, platinum catalysts, $n = 1$. Catalysts, however, do not affect equilibrium, and the equilibrium constant for a catalytic process corresponds to the molarity of the homogeneous non-catalytic reaction, and therefore

$$K = \frac{(C_{\text{SO}_2}^*)^2}{(C_{\text{SO}_2}^*)^2 C_{\text{O}_2}^*} \quad (2.19)$$

If a reaction is not a complex one and the coefficients of the chemical equation correspond to the reaction order, but one of the components is taken in a very large excess, there is no need to include its concentration in the kinetic equation, since the concentration practically does not change in the course of the reaction. For a reaction of the model



where $C_B \rightarrow 1$ (in mole fractions) it is convenient to employ and write kinetic equations in the form:

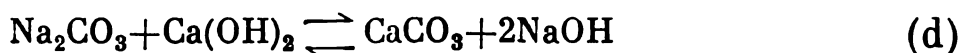
$$\vec{u}_1 = k'_1 C_A^m \quad \text{and} \quad \vec{u}_2 = k_2 C_D^p \quad (2.20)$$

where $k'_1 = k_1 C_B^n$; corresponding to this

$$K = \frac{k'_1}{k_2} = \frac{(C_D^*)^p}{(C_A^*)^m} \quad (2.21)$$

Rate constants and equilibrium constants are defined in this way, for example, for processes of hydrolysis, hydration, and formation of crystal hydrates, where a large excess of water is used.

For liquid-solid systems one other type of process is typical in which it is not necessary to include all the components in the kinetic equations. If a chemical reaction takes place in the liquid phase, but one of the reactants is of low solubility and is contained both in the liquid and in the solid phase, then its consumption in the reaction is accompanied by dissolving, and the concentration of the low-solubility substance in the liquid remains practically constant. Even if there is only a small excess of such a component, it should not be included in the equations to simplify calculations. An example is found in the reaction of causticizing a soda solution, employed in manufacturing (or regenerating) sodium hydroxide by the lime method. The reaction proceeds by



at a temperature of about 80°C and in an excess of lime, which is the less costly reactant. Lime is used in the form of milk of lime, which is a suspension of minute particles of $\text{Ca}(\text{OH})_2$ in its aqueous solution. The solubility of calcium carbonate is very low and as it is

formed and deposited out until the concentration of the sodium hydroxide rises to 100-130 g/dm³. According to the formal kinetics equation the equilibrium constant in the liquid phase should be given by

$$K = \frac{[\text{CaCO}_3^*] [\text{NaOH}^*]^2}{[\text{Ca(OH)}_2^*] [\text{Na}_2\text{CO}_3^*]} \quad (2.22)$$

However, taking into account the very large change in the concentrations of Na_2CO_3 ($C_{\text{Na}_2\text{CO}_3} \rightarrow 0$) and NaOH (from 0 to 120 g/dm³) and the comparatively insignificant change in the concentrations of Ca(OH)_2 and CaCO_3 in solution, the equilibrium constant of the reaction is determined for a given temperature from the equation

$$K' = \frac{[\text{NaOH}^*]^2}{[\text{Na}_2\text{CO}_3^*]}$$

where

$$K' = K \frac{[\text{Ca(OH)}_2^*]}{[\text{CaCO}_3^*]} = \text{const} \quad (2.23)$$

The equations for determining K_p values for gas-solid systems are simplified in the same manner.

For computing K_p standard tables contained in technical handbooks and textbooks on physical chemistry are often employed. They usually give the heat of formation (the change in enthalpy) q_p or ΔH (J/mole), the isobaric-isothermic potential of formation ΔZ , the change in free energy ΔF , and absolute entropy S at standard conditions, i.e. at a temperature of 25°C and pressure of 1 atm. For example

$$\log K_p = \frac{\Delta F}{19.1T} \quad (2.24)$$

or

$$\log K_p = \frac{T \Delta S - \Delta H}{19.1T} \quad (2.25)$$

However, for using equations (2.24) and (2.25) in computations the mechanism of the process must be known, i.e. not the overall, but the true reaction equations must be used.

The dependence of the equilibrium constant K_p on the temperature is expressed by the isobaric equation

$$\frac{d \ln K_p}{dT} = \frac{Q_p}{RT^2} \quad (2.26)$$

which is used for determining the unknown value of the equilibrium constant K_{p_2} at temperature T_2 from a known value K_{p_1} at T_1 and when the heat effect of the reaction at constant pressure Q_p is known in the form

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{Q_p}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2.27)$$

where R , equal to 8.32 J/mole · deg, is the universal gas constant. Substituting this value into (2.27) produces

$$\log \frac{K_{p_1}}{K_{p_2}} = \frac{Q_p (T_2 - T_1)}{19.1 T_1 T_2} \quad (2.28)$$

Equations (2.27) and (2.28) were obtained by integrating (2.26) for a constant value of Q_p (determined at T_1) and they are therefore valid only for a temperature interval in which there is also only a small change in the Q_p value.

For computing K_p when the changes in the temperature are large an equation of the following type is used:

$$\log K_p = \frac{q_p^0}{2.3RT} \pm \frac{\Delta a_0}{R} \log T \pm \frac{\Delta a_1}{4.6R} T \pm \frac{\Delta a_2}{13.8R} T^2 \pm K_{p_1} \quad (2.29)$$

Δa_0 , Δa_1 , Δa_2 , the coefficients in the Nernst heat equations, are given for various reactions in handbooks. Since the values of the coefficients $\Delta a_{0,1,2}$ are very small, in technical calculations simplified formulas are often used of the type

$$\log K_p = \frac{a}{T} \pm K_{p_1} \quad (2.30)$$

where $a = \pm \frac{q_p^0}{2.3R}$ (plus applies to exothermic reactions and minus to endothermic ones).

Equilibrium in heterogeneous systems, which determines the equilibrium yield of the product, depends on the temperature, the pressure and concentrations of the reacting substances. The values of the equilibrium constants of chemical reactions in each phase of a heterogeneous system are calculated using equations (2.5)-(2.30). Interphase equilibrium is based on the mass distribution law and phase rule (see Chapter V).

4. Rates of Technological Processes

The rate of a technological process with respect to the desired product depends on the rates of the forward reaction, the reverse reaction and of side reactions, and also on the rate of diffusion* of the reagents to the reaction zone and of the reaction products from that zone.

Using the laws governing equilibrium, one can only determine the maximum possible (theoretical) yield of the product. The theoretical yield, however, is usually not achieved in industrial processes, whose duration is limited because of the drop in the overall reaction rate

$$u = \overset{\rightarrow}{u_1} - \overset{\leftarrow}{u_2}$$

* Both molecular and turbulent diffusion.

as the concentrations of the starting materials drop. In irreversible processes, i.e. with $\bar{u} = 0$, the reaction rate approaches zero ($u \rightarrow 0$) when the supply of one of the initial reactants is depleted. In reversible processes $u \rightarrow 0$ when $\bar{u}_1 = \bar{u}_2$, i.e. when equilibrium is established. According to the mass action law, in an isolated system the amount of the product for a simple reaction of type (2.1) changes with time as described by the ascending logarithmic curve of Fig 1. The product yield x change is described by similar curve. The reaction rate, expressed as the amount of product obtained per unit time (the descending curve) u_1 , is large at the beginning of the process, but after some time τ_p the rate decreases to u_p . In irreversible processes the reaction rate approaches zero when equilibrium is approached or when the concentration of the starting materials drops. Naturally, it is not advantageous to carry out a production process at low rates and the process is, therefore, not continued to equilibrium. The curves of Fig. 1 approximately express the kinetics not only of chemical reactions but also of any interphase mass transfer process in a batch-type apparatus (for an isolated system) or in continuous-action apparatus where plug flow is approached.

The change in the concentrations of the principal initial material and of the reaction product during a process are given by curves which differ for simple and for complex reactions, and also for completely stirred and ideal plug-flow reactors. For simple processes which take place at ideal plug flow with no change in volume by the reaction mechanism $A \rightarrow D$ the concentration of the initial material C_A decreases in time (Fig. 2) from a value of C_{A_1} to zero for an irreversible process, or to the equilibrium value C_A^* for a reversible one. Correspondingly, the concentration of the product C_D grows for reversible processes from zero to the value C_D^* , which corresponds to the degree of conversion at equilibrium, i.e. to x_e , and for irreversible ones, to $x = 1$.

Most chemical reactions are complex, i.e. they are the result of several elementary reactions. The nature of the change in the reactant concentrations in the most simple case of a complex parallel reaction taking place in a plug-flow reactor, which can be illustra-

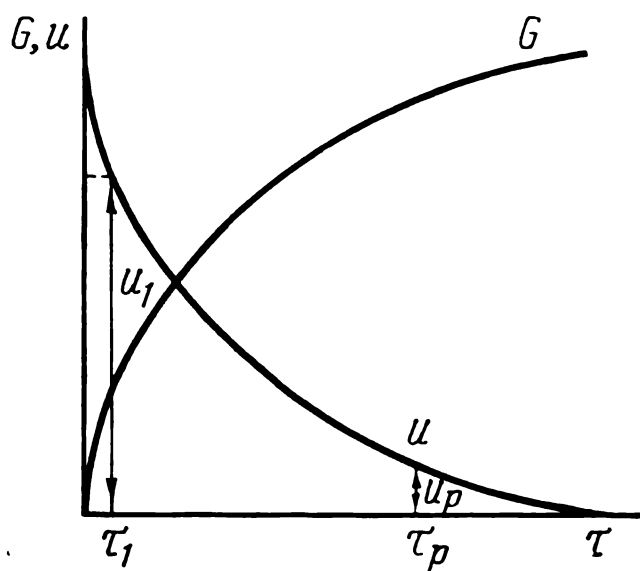
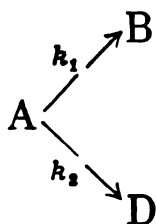


Fig. 1. Reaction kinetics of an irreversible process according to the law of mass action ($P, t = \text{const}$)

ted by



is shown in Fig. 3 (rate constant $k_1 > k_2$). For the simplest complex consecutive reaction of the type $A \xrightarrow{k_1} B \xrightarrow{k_2} D$ in an ideal plug-flow reactor the change in concentration is given in Fig. 4. In many industrial processes of organic technology the intermediate reaction product B is the desired product. As can be seen from Fig. 4, to obtain a maximum yield of B not only a large k_1/k_2 ratio, but also optimal processing time are necessary; any further increase in the processing time beyond the optimal value results in conversion of the desired product B into D. This is typical, for instance, for the many cases of oxidation used in manufacturing alcohols, aldehydes, acids and other

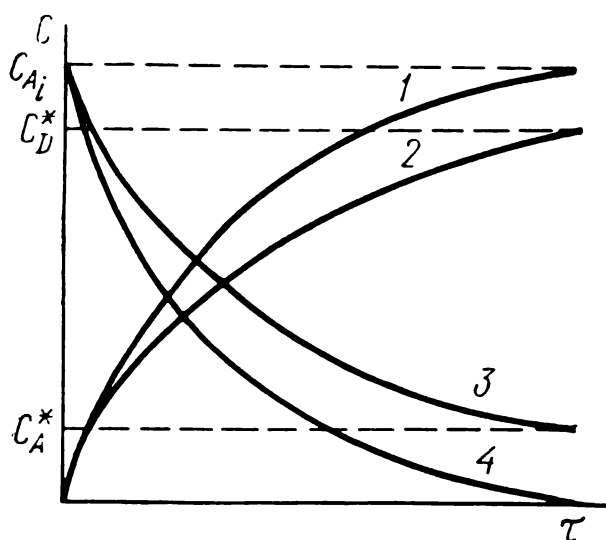


Fig. 2. Typical curves for change in concentration of reactants with time for simple reactions of type $A \rightarrow D$ in plug-flow reactors:

1, 2—growth in concentration of product D in irreversible and reversible processes; 3, 4—drop in concentration of the starting component

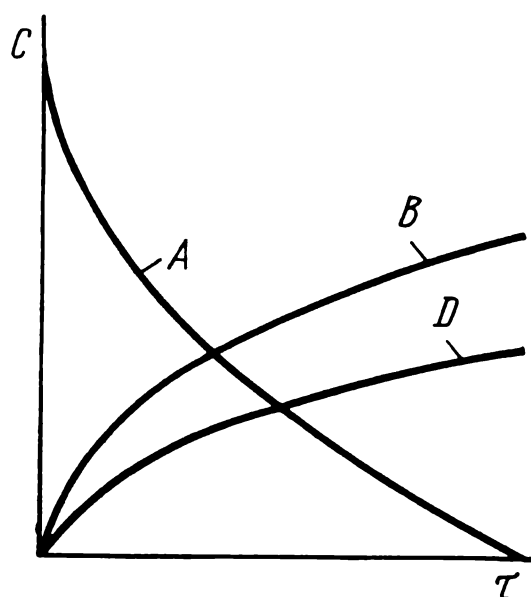


Fig. 3. Concentration changes in binary-parallel irreversible reactions

of type $A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} D \end{cases}$ with $k_1 > k_2$

oxygen derivatives of organic compounds, and also for partial hydrogenation (for example, $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$).

Since in a flow-through reactor the processing time τ is equal to the ratio of the height (length) of the reaction mixture H to the linear flow rate of the reactants w , or also to the ratio of the reaction mix-

ture volume V to the volumetric flow rate of the mixture V_m , i.e.

$$\tau = \frac{H}{w} = \frac{V}{V_m} \quad (2.31)$$

then for fixed values of w and V_m the curves of Figs. 1-4 also represent the relationships $C = f(H)$, $C = f(V)$, $u = f(H)$, $u = f(V)$, etc. The reaction kinetics curves, shown in Figs. 1-4, describe batch processes and ideal plug flow processes in flow-through reactors. Basic-

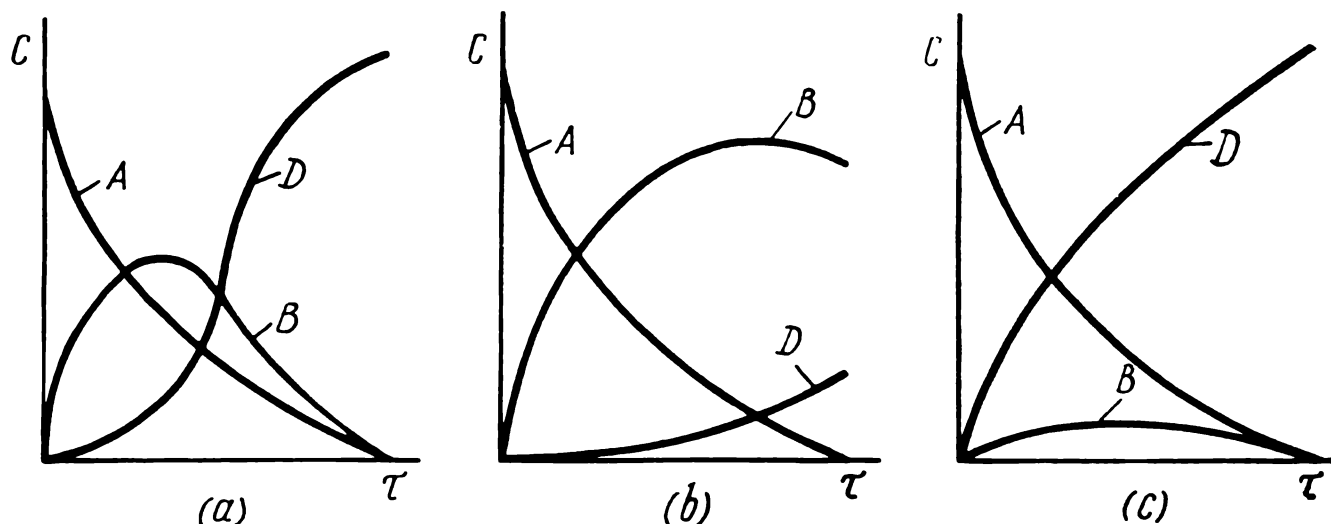
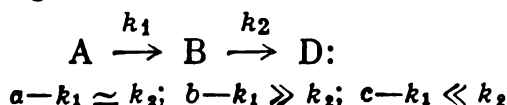


Fig. 4. Concentration changes in consecutive irreversible reactions of type



ly different are the kinetics curves of processes which approach the hydrodynamic regime of complete mixing (see the definition given on page 100). As can be seen from Fig. 5, at constant values of temperature t , pressure P and initial concentration C_i for processes in which stirring is almost perfect, the degree of conversion of the principal starting material*

$$x = \frac{C_{A_1} - C_{A_f}}{C_{A_1}} \quad (2.32)$$

for a certain given value of the reaction time τ_g is larger than in processes where there is no agitation of the reactants, i.e. which are diffusion controlled (curve 3). This is because the external diffusio-

* Equation (2.32) is only valid for processes at constant volume. If the volume is changed

$$x = \frac{C_{A_1} - \beta C_{A_f}}{C_{A_1}}$$

where β is a coefficient for referring the concentration to the initial volume of the reaction mixture.

nal resistance is removed in reactors with ideal stirring. On the other hand, the degree of conversion in conditions of complete mixing would be lower than in ideal plug flow for a kinetics controlled reaction (curve 2) at constant values of the process parameters ($t, P, C = \text{const}$). However, due to its very nature ideal mixing results in a constant temperature throughout the reactor volume equal to the end temperature of the product leaving the reactor; whereas in plug flow the temperature changes from inlet to outlet along an adiabatic straight line or polythermic curve.

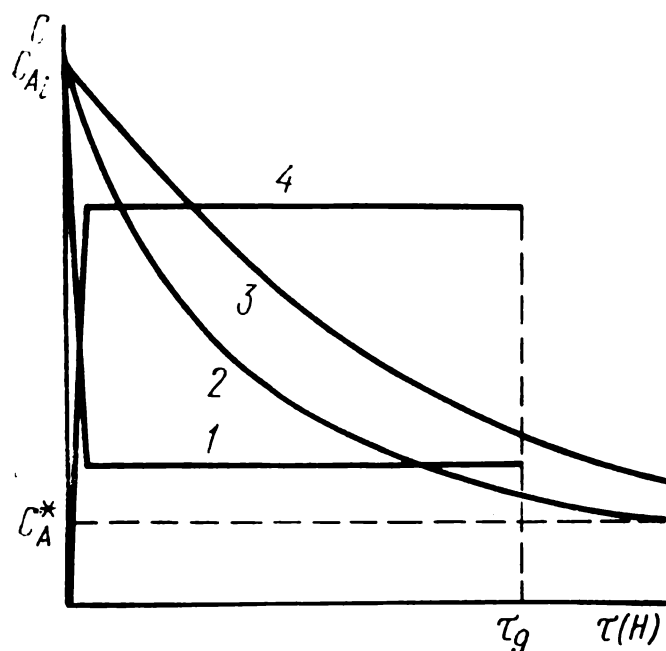


Fig. 5. Concentration change with time of process for a simple reversible reaction:

1—concentration of starting component C_A at close to completely mixed conditions and reaction time τ_g ; 2—concentration change of C_A in kinetics-limited plug-flow conditions; 3—concentration change of C_A in diffusion-limited plug-flow conditions; 4—product concentration, C_D , at close to completely mixed conditions

As a result, as will be shown below (see page 100), the mean temperatures and consequently the reaction rate constant may be lower than in completely mixed flow.

For all types of the flow pattern as the reaction time is increased the concentration of component A will approach the equilibrium value.

The rate of an industrial process determines the production capacity of the apparatus, or the required size and number. The process rate is calculated from the product yield x (see equation 2.8) at time τ or from the velocity coefficient of the process k . The yield can be expressed, depending on the conditions, either by the degree of conversion, the equilibrium yield or the actual yield.

The yield with respect to theory or the actual yield, x_a , shows how close the process has approached equilibrium and is the most important index for assessing the rates of industrial processes. The yield with respect to theory is the ratio of the actual amount of product obtained G_a to the amount which would be obtained at equilibrium G_e . The yield with respect to theory is always less than unity and it can only approach this limiting value.

The yield is often expressed as a percentage, for example,

$$x_a = \frac{G_a}{G_e} 100 = \frac{G_a}{G_{\max} x_e} 100 \quad (2.33)$$

For irreversible processes in formula (2.33) in place of G_e the value of G_t is used, i.e. the amount of product which would be obtained by